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Raman spectroscopic analysis of iron chromium oxide microspheres generated by nanosecond pulsed laser irradiation on stainless steel

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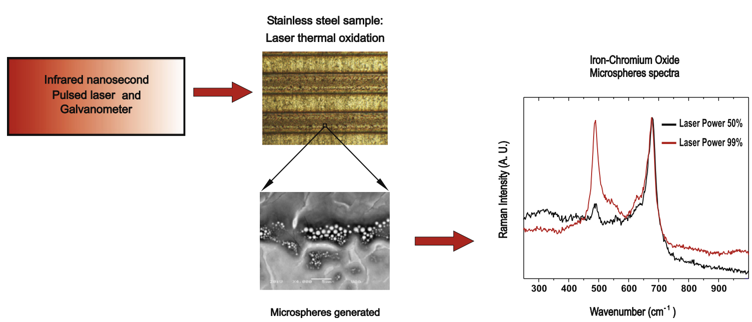
H I G H L I G H T S

- Generation of iron chromium oxide microspheres.
- Commercial stainless steel plates irradiated with an Ytterbium pulsed fiber laser.
- Raman spectroscopy analysis of iron chromium oxide microspheres.
- Energy-Dispersive X-ray Spectroscopy analysis of iron chromium oxide microspheres.
- Iron chromium oxide ratio is related to the applied laser power.

G R A P H I C A L A B S T R A C T



A R T I C L E I N F O

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Iron chromium oxide microspheres were generated by pulsed laser irradiation on the surface of two commercial samples of stainless steel at room temperature. An Ytterbium pulsed fiber laser was used for this purpose. Raman spectroscopy was used for the characterization of the microspheres, whose size was found to be about 0.2–1.7 μm, as revealed by SEM analysis. The laser irradiation on the surface of the stainless steel modified the composition of the microspheres generated, affecting the concentration of the main elemental components when laser power was increased. Furthermore, the peak ratio of the main bands in the Raman spectra has been associated to the concentration percentage of the main components of the samples, as revealed by Energy-Dispersive X-ray Spectroscopy (EDS) analysis. These experiments showed that it is possible to generate iron chromium oxide microspheres on stainless steel by laser irradiation and that the concentration percentage of their main components is associated with the laser power applied.

Introduction

The search for novel methods to synthesize iron oxide micro and nanoparticles is in continuous development, mainly due to their importance in various industrial fields and their scientific interest. Some of their uses are in the food industry, chemical coatings, catalysts, biochemical sensors and medical devices, among others [1–5]. These particles have new and novel properties that are being extensively studied in order to find new and better applications.

Iron chromium has been studied due to its improved catalytic effects in certain reactions when compared to Fe or Cr catalysts by themselves and the synthesis of iron and chromium oxides

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has been extensively reviewed [6–8]. The main methods used to synthesize iron and chromium oxides are physical, chemical and biological. Among the chemical methods, the thermal decomposition method offers improved control over the size and shape of iron oxide nanoparticles, which depends on the precursor and temperature [9–10].

One of the physical methods is laser thermal oxidation, a relatively new technique where most of the parameters involved are controlled in order to generate the appropriate oxide (with novel structures) on the surface of metallic materials [11–13]. Moreover, thermal effects can generate different microscopic morphologies and different phases on the surface of the samples, resulting in changes in the properties of the surface [14–15]. One of these changes involves the formation of spherical particles, mainly due to the heating effect generated on the surface by the focused laser and parameters such as scan speed, laser power, pulse width and frequency, among others. These particles are randomly generated by the heat induced by the laser spot and randomly distributed over the laser interaction zone; their composition depends on the original elemental composition of the sample, according to the elements with higher weight percentage (wt%) that are distributed over the surface. The size of these particles ranges from hundreds of nanometers to a few microns.

In a previous work, Ortiz-Morales et al. conducted an experimental study on the generation of micro iron-oxide zones in order to identify the micro-oxide areas produced by laser irradiation on stainless steel plates [16]. There were some doubts regarding the Raman spectra of a particular area that presented two main Raman bands at 488 and 675 cm^{-1}; thus, it was carried out a study on the evolution of the oxide generated in this area and found its Raman spectrum as a function of laser power. This experiment allowed us to find that this oxide area was composed of a thin film of iron chromium oxide attached to the sample surface and microspheres (MS) of different sizes grouped in clusters.

The purpose of this work was to analyze the microspheres generated by a focused spot laser on the surface of stainless steel plates, to characterize the effect of laser power in the microspheres and to find the correlation between the main components of the sample and the laser power applied.

Experimental setup

Two samples of commercial stainless steel plates with a thickness of 2 mm were used in this experiment, SE304 and SE430; they were cut into pieces with dimensions of 25 × 50 mm, cleaned with deionized water and dried in air.

For irradiation, the samples were mounted on a fixed table at the focal length of the F-theta lens of an Ytterbium pulsed fiber laser (IPG Photonics, model YLP-1-100-30-30-HC) with a beam focused diameter of about 55 μm, an average output power of about 30 W and a wavelength of 1064 nm. The samples were irradiated using 10–99% of the maximum laser power (5 and 29 W of average power, respectively) in 10% increments of laser power on ten 6 mm squares, a square for each percentage value. The width and repetition rate of the laser pulse used for irradiation were about 120 ns and 80 kHz, respectively. Each marked square had a hatch pattern, with spacing between lines of 0.2 mm. The laser scan was done using a scanning speed of 80 mm/s and three scanning cycles. Laser power was measured using a Gentec Power Meter model UNO and a power detector model UP19K-150W-H5.

The Raman spectra of the microspheres were measured using a Micro-Raman (Renishaw system 1000B) with a 600 lines/mm grating, a CCD camera (Rem Cam 1024 × 256 pixels), focusing its 830 nm wavelength laser beam (with a spot-size of about 2 μm) in a back scattering geometry onto the sample [17], using the 50× objective of a Leica (DMLM) microscope. The instrument was calibrated using the 520 cm^{-1} Raman line of a silicon wafer. For data acquisition, Grams software was used. Measurements were made at several points in each area where the microspheres were present and along several lines for each marked square for every value of laser power applied. A representative spectrum is shown here. The Raman spectra were normalized to the most intense peak, without any previous base line correction or smoothing.

The elemental composition of the microspheres was determined with Energy-Dispersive X-ray Spectroscopy (EDS), by using a Scanning Electron Microscope system (SEM, JEOL JSM-5900LV). The SEM system was also used to measure the size of the microspheres. All measurements were made on the sample surface, in the zones with microspheres.

Results

Samples before irradiation

Using the EDS elemental analysis, the main components of the samples were determined, that is, those with the highest concentration in each sample, and it was found that both samples contained mostly Cr and Fe. Table 1 shows the weight% of the components of the samples, denoted as S1 for SE304 and S2 for SE430.

Irradiated samples

For 10% and 20% of laser power, there were no visible laser effects on the samples, neither with the SEM system (not shown). Fig. 1 shows SEM images of a section of sample S1, where the marked pattern can be observed, as well as a detail of the main laser interaction zone, in this case for 50% of laser power. Fig. 2 shows SEM images of the laser irradiated sample S1, from 30% to 99% of laser power. With 30%, a laser heat-affected zone began to appear, and with 40% there was a clear visible laser effect on the sample surface; however, there were no visible features, as it can be observed in Fig. 2a and b, respectively. With 50%, some features began to appear throughout the main laser interaction zone in all the lines of the marked pattern. From the SEM images it can be observed that these features seem like microspheres (MS), as is shown in Fig. 2c. The generated microspheres can be clearly seen starting from 50% to 99% of laser power.

The EDS analysis showed that the laser-affected zones without microspheres (see Fig. 2a and b) vary mainly with respect to the percentage composition of O, Cr and Fe; this can be observed in Table 2. For 30% and 40% of laser power, there was an increase of oxygen and chromium, but iron content decreases. It is worth mentioning that the EDS measurements were done at the center of the laser heat-affected zone. From 50% to 99% of laser power, the chromium content of the microspheres increases as laser power increases, while iron content decreases. Certainly, the presence and variation of oxygen content implies that there is an oxide.

It is also remarkable the way in which the microspheres began to arrange themselves along the scanning direction of the laser at the edge of the main laser interaction zone (see Fig. 2d). This is

Table 1
EDS analysis of the elemental composition of stainless steel samples S1and S2 before laser irradiation (elements with higher wt%).

Sample	Elements		
	Cr	Fe	Ni
	wt%		
S1	17.33	68.71	7.63
S2	15.85	80.28	–